A Kinetic Study on Sulphation of Sodium-Based Porous Solid Reactant with Flue Gas

A Thesis Submitted

in Partial Fulfillment of the Requirements
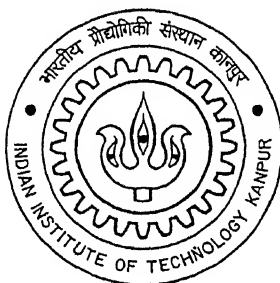
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By

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Indian Institute of Technology, Kanpur

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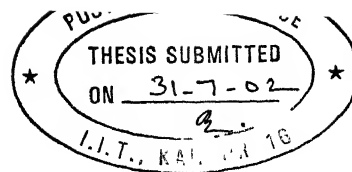
CERTFICATE

It is certified that the work contained in the thesis entitled "*A Kinetic Study on Sulphation of Sodium-Based Porous Solid Reactant with Flue Gas*", by Mr. Pawan Kumar Agrahari, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

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ABSTRACT

Kinetic data of the sulphation reaction of the sodium-based porous solid reactant with flue gas were obtained from experiments in a thermogravimetric set-up under different process variables such as temperature, sulphur dioxide concentration and exposure time. The kinetic and other parameters were determined on the basis of the grain model reported in literature. The Experimental study verified that the sulphation reaction was of first order with respect to sulphur dioxide concentration. The conversion was found to increase up to a temperature of 300 °C and beyond that it decreased. The intrinsic rate constant (k) was found to vary from 1.24×10^{-4} to 3.75×10^{-4} cm/s in the temperature range of 150 to 250 °C. The activation energy (E) and frequency factor (A) were found to be 4368 Cal/mole and 0.0217 cm/s respectively. The effective diffusivity (D_e) varied from 8.9×10^{-3} to 18.7×10^{-3} cm^2/s in the temperature range of 150 to 250 °C. Comparison of predicted conversion of the solid reactant with experimental data indicated that the sulphation reaction follows chemical reaction model for a short initial period, and then matches well with the pore diffusion model with the progress of reaction.

ACKNOWLEDGEMENT

CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

A   Frequency factor

A_g Surface area of grains of solid reactant, cm^2/gm

A_p Surface area of pellet, cm^2

C   Concentration of SO_2

D_e Effective diffusivity, cm^2/s

E   Activation energy, kCal

F_g Grain shape factor

F_p Pellet shape factor

ΔH_f Enthalpy change, kCal

k   Intrinsic reaction rate constant, cm/s

n   Order of reaction

R   Universal gas constant

t   Time of reaction

t^* Dimensionless reaction time, $bkC(A_g/F_gV_g)t/\rho$

T   Temperature, K

V_g Volume of grains of solid reactant, cm^3/gm

V_p Volume of pellet, cm^3

X   Fractional conversion

Greek Symbols

ε_o Initial porosity

ρ Density of solid reactant, $g\text{-}mole/cm^3$

σ Reaction modulus

1. INTRODUCTION

Sulphur dioxide is a major anthropogenic gaseous air pollutant. It is released into the atmosphere through various sources including power plants, sulphuric acid plants, petroleum refineries, and metal smelters. A great deal of attention has been given in recent years to the problem of reducing the level of atmospheric pollution caused by sulphur dioxide emissions because it causes several adverse effects on environment and human health. The various methods for abating sulphur dioxide emissions include burning of low sulphur fuel, removal of sulphur from fuel, substitution of another energy source, cleaning up of the combustion products containing sulphur dioxide as far as possible from source and eventual dispersion through stacks. Among various control methods, cleaning up of flue gases has received maximum attention.

The problem of sulphur dioxide removal from flue gases has probably been the subject of more research than any other gas purification process. The phenomenal growth of using different scrubbing processes on commercial scale had started in seventies due to regulatory pressures in various countries. Prior to 1980 the removal of sulphur dioxide from flue gases was usually carried out by conventional wet scrubbing process. It is an efficient but a costly process involving huge capital and operating cost. As an alternative to this, dry scrubbing was developed as a low cost option with additional advantage of eliminating sludge handling problems (Muzio and Offen, 1987). Attempts have been made to use various porous solid reactants that remove sulphur dioxide by chemical reaction, adsorption, catalytic reaction or a combination of processes. Though a variety of porous solid reactants were found to remove sulphur dioxide from flue gases under dry conditions, only a few of them are in commercial use. These include calcium, magnesium, and sodium based reactants. The sulphur dioxide removal by dry process can be improved by developing a better understanding of the process with commercially available reactants, modified or new reactants, and modified process. Extensive

investigations are necessary to develop a better understanding of the process using the available reactants so that removal potential of sulphur dioxide can be increased.

Sodium bicarbonate, when injected into hot gas streams, will decompose leading to the formation of sodium carbonate. The freshly obtained sodium carbonate is highly porous and therefore extremely reactive. The objective of the present study is to examine the reactivity of this sodium-based porous solid reactant with sulphur dioxide in flue gas and to determine the kinetic and mass transfer parameters of the sulphation reaction under various process variables. These parameters can be used to predict the performance of this porous solid reactant in different dry scrubbing systems prior to actual pilot scale testing.

2. BAKGROUND INFORMATION

The major cause of air pollution is combustion, and combustion is essential to man. Impurities in fuel cause the formation of side products such as oxides of sulphur, oxides of nitrogen, fly ash and unburnt hydrocarbons.

2.1 OXIDES OF SULPHUR AND SOURCES

In general there are six different oxides of sulphur in the atmosphere viz. Sulphur monoxide (SO), sulphur dioxide (SO_2), sulphur trioxide (SO_3). Sulphur tetraoxide (SO_4), sulphur sesquioxide (S_2O_3) and sulphur heptoxide (S_2O_7) (Peavy et al., 1986). However, only sulphur dioxide and sulphur trioxide are of prime importance in air pollution study, as they constitute more than 99% of total sulphur oxide emission (Stern, 1977). In the combustion of fossil fuels, the SO_2/SO_3 ratio is typically 40:1 to 80:1 (Wark and Warner, 1981). Monitoring of sulphur compounds in the atmosphere is usually restricted to the dominant gas, sulphur dioxide.

The sources of sulphur dioxide can be sorted as natural and anthropogenic. The natural sources are forest fire, volcanic eruptions and conversion of hydrogen sulphide into sulphur dioxide in the atmosphere. Moreover, anthropogenic sources are of prime importance from the pollution control point of view. Sulphur is a component of all natural oil and coal with a composition varying from 0.1 to over 5.0 percent. Thus the total emission of sulphur dioxide varies considerably with the nature or the origin of fossil fuels. Out of all anthropogenic sources, it is found that the combustion of fossil fuels contributes to above 80% sulphur emission (Wark and Warner, 1981). Fuel combustion in stationary sources and industrial processes are the principal contributors of sulphur dioxide. However, there are some other sources of SO_2 also, such as refining of petroleum, manufacturing of sulphuric acid, burning of refuse, smelting of ores containing sulphur. A little amount of SO_2 is also contributed by transportation because the sulphur content of gasoline is very low (about 0.03% by mass). (Peavy et al., 1986).

A brief information regarding the contributors of SO$_2$ by various sources is given in table 2.1

Table 2.1: Various sources and their contribution to sulphur Dioxide

Sources	Contribution to SO$_2$
Combustion of fossil fuels for power generation	46%
Other combustion of coal and petroleum products	32%
Smelting of ores	12%
Miscellaneous sources	4.6%

Source: Hangebrauck and Spaite, 1986

2.2 EFFECT OF SULPHUR DIOXIDE ON ENVIRONMENT

Sulphur dioxide is a colourless, non-flammable, non-explosive gas that causes a taste sensation at concentration from 0.3 to 1.0 PPM in air. At concentration above 3.0 PPM the gas as a pungent, irritating odour. As per ambient air quality standards, the sulphur dioxide concentration should not exceed 80 $\mu g/m^3$ for industrial area, 60 $\mu g/m^3$ for a residential area and 20 $\mu g/m^3$ for sensitive area with and averaging time of 8 hours. Sulphur dioxide is partly converted to sulphur trioxide or to sulphuric acid and sulphate salt by photochemical or catalytic processes in the atmosphere. The oxides of sulphur in combination with particulate and moisture produce the most damaging effects attributed to atmospheric air pollution (Wark and Warner, 1981). A brief account of various effects of sulphur dioxide on the environment is given below.

2.2.1 Effects on Human Health

Sulphur dioxide, sulphuric acid and sulphate salt tend to irritate the mucous membrane of the respiratory tract and foster the development chronic respiratory diseases, particularly bronchitis and pulmonary emphysema.

2.2.2 Effects On Vegetation

Different species and variety of plants vary in their sensitivity to sulphur dioxide exposures. Alfalfa is most sensitive species with acute injury observes at a dose of 1 PPM for 1 hr (Godish, 1985). Sulphur dioxide enters stomata of livers and immediately comes in contacts with spongy mesophyl cells in the vicinity of the pore, where the toxic response is initially manifested, and with time there is a progressive expansion of injury and tissue collapses. The injury caused to leaf by sulphur dioxide may lead to plant damage and loss of crop yield. (Peavy et al., 1986).

2.2.3 Effects On Materials

Available literature shows that sulphur compounds are responsible for major damage to materials. Increase of sulphur dioxide concentration in the atmosphere drastically increases the drying time of paint film. Sulphur dioxide generally accelerates metal corrosion by first forming sulphuric acid either in the atmosphere or on the metal surface. Sulphuric acid is capable of attacking a wide variety of building materials including limestone, marble, roofing, slate, and mortar. Sulphur oxides are considered to cause the loss of tensile strength of nylon and cotton fabric (Stern et al., 1984).

2.2.4 Effect On Statues and Historic Monuments

Acid deposition caused by sulphur and nitrogen emission from the burning of fossil fuels is causing a significant damage to magnificent historic buildings. The victims of this destructive process all over the world makes up a long list. There are many such instances in India also. The famous widely known episode is that of Taj Mahal being affected by the sulphur dioxide emitted from the Mathura Refinery and several small scale industries like foundries in and around Agra.

2.2.5 Effects on Visibility

One of the major products of the photochemical reactions between sulphur dioxide, particulate matter, oxides of nitrogen and hydrocarbons in the atmosphere is the light scattering droplet of sulphuric acid mist. Since aerosols of sulphuric acid and other sulphates make up 5 to 20 percent of the total suspended particulate matter in urban air, they contribute significantly to the reduction in visibility (Peavy et al., 1986).

2.2.6 Acid Rain

When sulphur dioxide and NO_x present in the atmosphere absorbed in cloud water and raindrops, they are transformed to acids. A typical reaction might be:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$
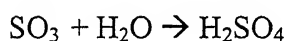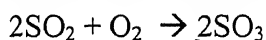
These acid aerosols are then deposited in significant quantities on the surface of land and water. Such a phenomenon is called acid rain.

The increasing presence of acids is attributed to the increase in emissions of sulphur dioxide and NO_x. There are several effects of acid rain that are disturbing. Firstly there is an acidification of natural water sources. This can have a devastating effect on fish life. Secondly, a leaching of nutrients occur in the soil. This demineralization can lead to loss in productivity of crops and forest or a change in the natural vegetation.

2.3 SULPHUR DIOXIDE CONTROL TECHNOLOGIES

The technical and economic feasibility of an SO_2 removal process depends on the type and the quantity of effluent that must be cleaned. Removing the sulphur from fuel or remaining SO_2 from exhaust gases are two basic approaches to SO_2 emission control. The later one is most widely practiced.

Four possible methods or alternatives may be used to reduce sulphur dioxide from fossil fuel combustion include

A.   Change to low sulphur fuel such as

    i.   Natural gas,

ii.   Liquefied natural gas,

iii.   Low-sulphur oil, and

iv.   Low-sulphur coal.

B.   Use desulphurised coal and oil.

C.   Use flue gas desulphurisation (FGD) system.

D.   Tall stack dispersion of the SO_2 remaining after FGD (for meeting the ambient standards).

2.3.1 Flue Gas Desulphurisation Systems

Flue gas desulphurisation is presently the most commonly used technology to comply with SO_2 requirement (Chu and Rochelle, 1999). The post furnace combustion control processes currently achieve the highest level of SO_2 removal.

FGD processes may be grouped according to two classifications:

i. Throwaway or regenerative, and

ii. Wet or dry.

Throwaway processes are those in whish the water products formed is discarded. As a result, fresh chemicals also must be continually added. In regenerative processes, as the name implies, the chemistry is such that the removal agents can be continually regenerated in a closed-loop system. The wet methods employ a slurry or solution of some adsorbent for SO_2 removal, whereas the dry system use dry particles of adsorbents in such gas-solid contacting devices such as fluidized beds, packed beds, and entrainment reactors. The removal system typically involves the use of absorption, adsorption or catalytic processes. In FGD systems, the throwaway process is found to be cheap and less complex than the regenerable one (Ghosh et al., 1988).

2.3.2 Dry Process

The use of dry sorbent for emission control is not a new one, having been extensively investigated in the late 1960's and 1970's. However, the technology was not pursued or implemented due to optimistic performance and cost projections of wet FGD systems and regulatory requirements for 90% sulphur dioxide reduction (viz., in USA) which was (and still is) beyond the capability of dry sorbent injection for controlling SO_2.

Recently interest in dry SO_2 removal processes has been renewed due to successful implementation of this process in Germany and the need for a low cost sulphur dioxide control technology (Muzio and Offen, 1987).

Dry injection processes involve the injection of dry sorbent powders into either the furnace or post furnace region. The dry powder exposed to the pollutants is subsequently removed in the particulate collectors installed downstream. The primary advantage of pulverized dry sorbent addition over conventional wet scrubbing are its lower cost, the ease with which it can be retrofitted into existing boilers, the attractiveness of product and the reduced space requirements (Newton and Norman, 1997).

Presently four general approaches are available or under development for bringing sorbent into contact with the SO_2 (Muzio and Offen, 1987):

i.   Furnace injection of calcium base compounds.

ii.   Economizer injection of calcium hydroxide.

iii.   Post furnace injection of calcium hydroxide into combustion products at a high relative humidity.

iv.   Post furnace injection of sodium based sorbents

Dry process can be effectively used in India for the removal of sulphur dioxide because of its low sulphur content.

2.4 SULPHATION REACTION OF SODIUM-BASED REACTANTS

It has been recognized that reactions involving porous solids are very important. It is now accepted that such structural parameters as the porosity, specific surface area, and pore size distribution of the solid reactant will markedly affect the rate of reaction. (Szekeley et. al; 1976). Sulphur dioxide removal is often carried out by porous solid reactants which may be calcium, sodium, or magnesium based, etc. The removal of sulphur dioxide by lime was found to be very high because of its high porosity (Pigford and Slifer, 1973).

The use of sodium bicarbonate ($NaHCO_3$) as solid sorbent for the removal of sulphur dioxide from flue gases has many attractive features, including a high degree of conversion, and process simplicity when coupled with a fabric filter.

The overall reaction of sodium bicarbonate with sulphur dioxide in a flue gas has the following form (Erdos et al., 1989):

$$NaHCO_3 + SO_2 + \frac{1}{2} O_2 \rightarrow Na_2SO_4 + 2 CO_2 + H_2O \qquad (2.1)$$

$$\Delta H_f = -69.66 \text{ kcal}$$
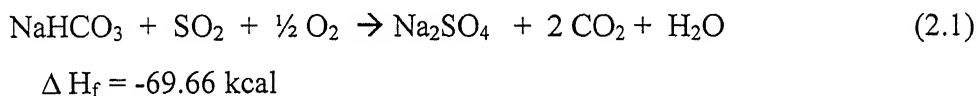
However it has been assumed by previous researchers that sodium carbonate does not react directly with sulphur dioxide, but the product of its thermal decomposition does. Thermal decomposition of sodium bicarbonate above 115°C is reasonably fast at atmospheric pressure yielding sodium carbonate (Keener and Davis, 1984).

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \qquad (2.2)$$

The sodium carbonate reacts readily with sulphur dioxide in the presence of sodium sulphate according to the reaction

$$Na_2CO_3 + SO_2 + \frac{1}{2} O_2 \rightarrow Na_2SO_4 + CO_2 \qquad (2.3)$$

$$\Delta H_f = -76.45 \text{ kcal}$$
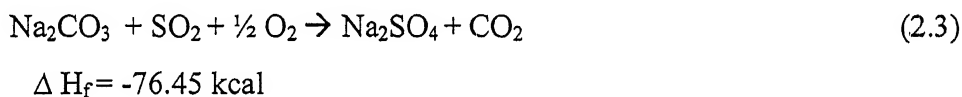
From the above reaction [Equation (2.2)] one can see that when two molecules of sodium bicarbonate decompose on heating, one molecule each of carbon dioxide and water are released. Hence the freshly obtained sodium carbonate is highly porous and reactive toward sulphur dioxide. It should be noted that the extremely high reactivity is a feature of only those anhydrous sodium carbonates, which are prepared by thermal decomposition of parent substances containing the HCO_3^- ion (e.g., sodium bicarbonate). Other sodium salts containing only the CO_3^{2-} ion, especially hydrates of sodium carbonate, yield by the dehydration at elevated temperature, anhydrous sodium carbonate, which is almost unreactive toward sulphur dioxide. The results of a pilot plant dry scrubbing study also indicated the superiority of use sodium bicarbonate as a sorbent over normal sodium carbonate (Keener and Khang, 1993).

2.5 MODEL FOR GAS-SOLID REACTIONS

The sulphation of any solid reactant is a heterogeneous gas-solid reaction involving a moving boundary. A model is aimed at introducing structural features into reaction scheme.

The model to be presented here is based on the work of Sohn and Szekely (1972) called Grain model. This model considers the solid reactants to consist of uniformly sized particles of specific shape forming together as a pellet.

The sulphation of solid reactants may be described by the general reaction equation.

$$A (g) + bB(s) \rightarrow cC (g) + dD (s) \qquad (2.4)$$
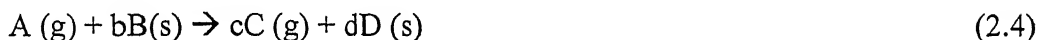
The overall volume of solid may increase or decrease depending on the relative density of solid product compared with that of the solid reactant. In most cases however the change is rather small and the overall size may be regarded as constant. When the solid reactant is porous there is a gradual change in the degree of conversion throughout the particle. The external layer will be completely reacted after some time and the thickness of this completely reacted layer will increase towards the interior of the particle. Under these conditions the reaction within the partially reacted zone occurs simultaneously with diffusion of gaseous reactant in this zone.

When chemical reaction presents the major resistance to the overall progress of the reaction, the concentration of the fluid reactants will be constant everywhere and reaction will occur uniformly throughout the volume of the solid. If on the other hand pore diffusion presents the major resistance, the reaction will occur in a narrow boundary between the unreacted and the completely reacted zones where the gaseous reactant concentration becomes zero. In the intermediate region where the resistance presented by chemical reaction and pore diffusion are of comparable magnitude both processes must be considered simultaneously.

To develop the mathematical relationship describing the reaction of a porous solid in terms of the generelised grain model , the following assumptions were made:

1. The pseudo steady state approximation is appropriate for describing the concentration of the gaseous reactant within the pellet.

2. The resistance due to external mass transport is negligible.

3. The solid structure is macroscopically uniform and is unaffected by the reaction.

4. The system is isothermal.

5. The effective diffusivity of gaseous reactant and product are equal and uniform throughout the pallet.

6. Diffusion of the gaseous reactant through the product layer of the individual grain does not affect the rate.

2.5.1 Chemical Reaction Model

The situation occurs when the rate of diffusion through the interstices among the grains presents negligible resistance to the progress of reaction and thus chemical kinetics controlled the process. Such a system may be considered as an agglomerate of individual grains reacting in the absence of mass transport resistance. Thus the concentration of the gaseous reactant is uniform throughout the solid. The grains are assumed as non-porous and within each grain the reaction front retains its geometric shape as reaction proceeds. For an nth order reaction it can be written as (Sohn and Szekely, 1972)

$$t^* = g_{F_g}(X) \equiv 1 - (1-X)^{\frac{1}{F_g}} \qquad (2.5)$$

Where t^* = Dimensionless reaction time, $\dfrac{bkCA_g}{\rho F_g V_g} t$

C = concentration of SO_2 , g-mole/cm^3

t = time of the reaction (exposure time)

b = stoichiometric coefficient

k = intrinsic rate constant

ρ = density of the solid reactant, g-mole/cm^3

A_g = surface area of the grains of the solid reactant

V_g = volume of the grains of the solid reactant

F_g = grain shape factor

The grain shape factor has values 1,2 and 3 for flat plates, long cylinders and spheres, respectively. This relationship enables one to determine from experimental conversion data the intrinsic reaction rate constant.

2.5.2 Pore Diffusion Model

If the chemical reaction step presents a negligible resistance to the progress of reaction, compared with the resistance due to pore diffusion, the overall rate is controlled by pore diffusion. In this case the reaction occurs in a narrow separating the unreacted core and the completely reacted layer where the reactant concentration drops to a very small value. Under this condition it can be written as (Sohn and Szekely, 1972):

$$t^* = \sigma^2 p_{F_p}(X) \tag{2.6}$$

where $p_{F_p}(X) \equiv X^2 \; for \; F_p = 1$

$$\equiv X + (1-X)\ln(1-X) \; for \; F_p = 2$$

$$\equiv 1 - 3(1-X)^{\frac{2}{3}} + 2(1-X) \; for \; F_p = 3$$

and σ is a characteristic parameter called reaction modulus

$$= \frac{V_p}{A_p}\left[\frac{(1-\varepsilon_0)k}{2D_e}\frac{A_g}{V_g}\frac{F_p}{F_g}\right]^{\frac{1}{2}}$$

An estimate of modulus σ might provide enough information as to whether one needs data on chemical kinetics or diffusion or both in order to predict the relationship between conversion and time. If σ is much smaller than unity only kinetic parameters are required; if it is much larger than unity only diffusion parameters are required. If σ is around unity both will be required.

The effective diffusivity can be determined by plotting according to Eq. (2.6) the conversion data obtained under conditions of diffusion control. While it would be desirable to conduct independent measurement of effective diffusivity, the procedure outlined here provides a convenient means of ascertaining whether the independent measurements are in fact consistent with the experimental data.

3. OBJECTIVE OF THE PRESENT STUDY

The present investigation deals with an experimental study of the reaction between a sodium-based porous solid reactant (sodium carbonate obtained by thermal decomposition of sodium bicarbonate pellet) and sulphur dioxide present in flue gas, prepared synthetically in laboratory. The objective is to determine the kinetic and mass transfer parameters of the sulphation reaction.

A laboratory study is conducted by thermogravimetric method under different process variables such as temperature, sulphur dioxide concentration, and exposure time. The related data are used to assess the effects of these process variables on sulphation reaction, and to evaluate the kinetic and mass transfer parameters of the reaction. It is expected that these parameters may be useful to predict the performance of the solid reactant in various dry flue gas desulphurisation systems.

4. MATERIALS AND METHOD

Laboratory experiments were conducted to generate the data for sulphation of solid reactant under various experimental conditions. Thermogravimetric technique was used in which weight change data were recorded under different conditions.

4.1 MATERIALS

Sodium bicarbonate taken in powder form (for making pellets) was of laboratory reagent grade, manufactured by Loba Chemie Pvt. Ltd., Mumbai. All the glassware used in the experiment were of 'Pyrex' quality, manufactured by Borosil Glass Works Ltd., Mumbai. Water used in the work was laboratory made distilled water.

4.2 EXPERIMENTAL SET-UP

Fig. 4.1 presents schematic diagram of Thermogravimetric set-up. It consists of a vertical furnace, an inconel tube as reaction chamber, a glass jacket, gas inlet and outlet pipes, thermocouple for measurement of temperature, sample suspending assembly consisting of nichrome wire and a stainless steel basket, and a single pan balance with readability of 0.01 mg for continuous reading of instantaneous weight.

A kanthal wound vertical furnace of 53-cm length was used in the study for maintaining the temperature. An inconel tube of 80-cm length and 5 cm internal diameter was employed as the reaction chamber. The inconel tube reaction chamber was fitted with a brass flange at the bottom to provide tight fitting cover. At the top a separate arrangement was made for the outlet of flue gas so as to prevent it from escaping into laboratory environment through the opening provided for suspending the steel basket from the balance. The flue gas was pumped out through the outer chamber using a suction pump thus preventing the escape of flue gas through the inner chamber into the laboratory environment.
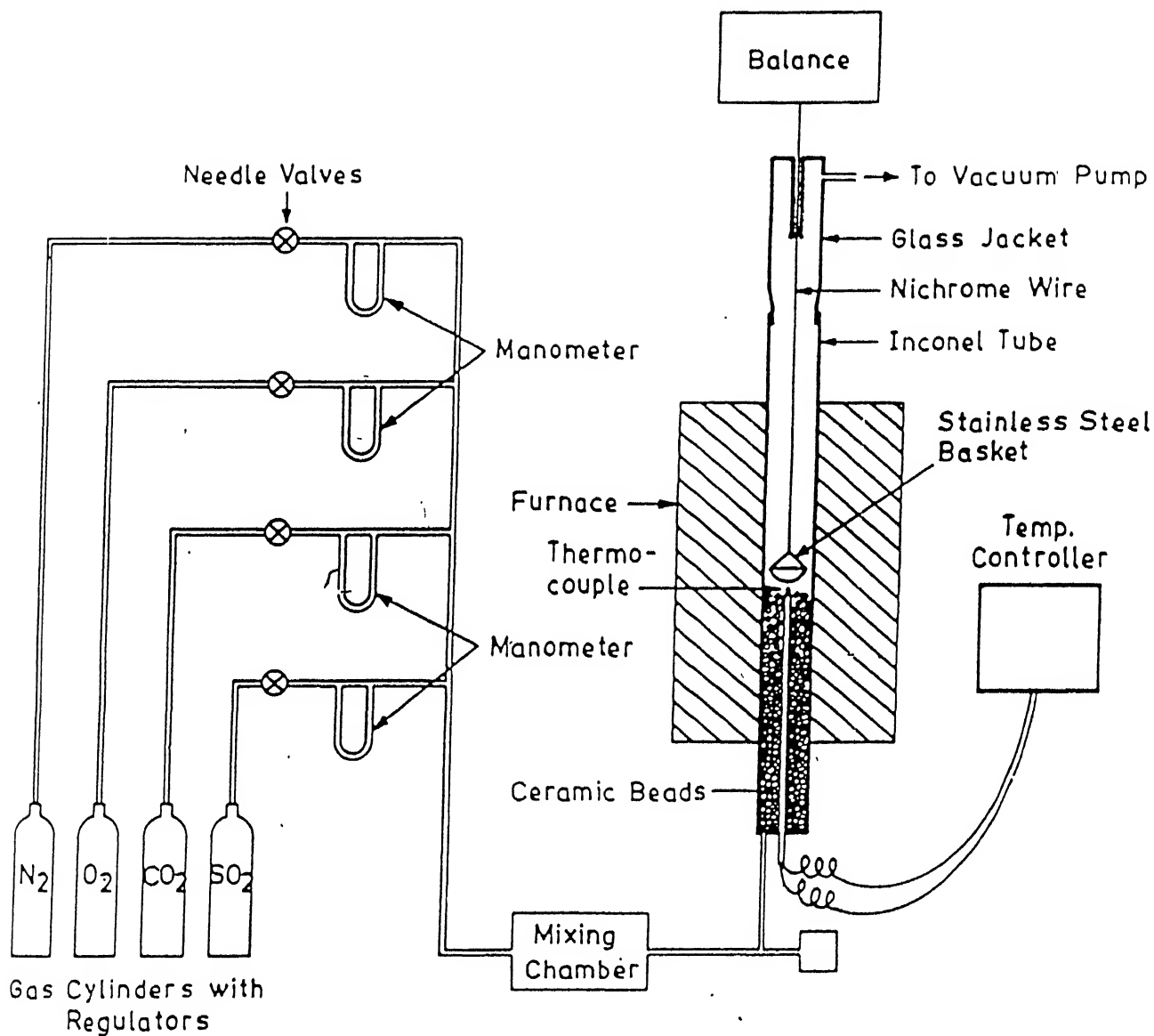
Fig. 4.1 Experimental set-up for Thermogravimetric Analysis

4.3 PREPARATION OF PELLETS

About 3.0 gm of dry sodium bicarbonate powder was taken and put in a cylindrical die of diameter 13 mm. The height of pellet was kept equal to diameter so as to get approximately spherical pellets. The die was subjected to a force of 2000 kg by a hydraulic press. The pellet was taken out and stored in a desiccator till the beginning of experiment.

4.4 PREPARATION OF FLUE GAS

The flue gas was prepared by mixing the individual gaseous constituents from four gas cylinders containing pure nitrogen, oxygen, and carbon dioxide and sulphur dioxide. The flow of individual components were controlled and measured with manometers connected with capillary tubes. The flow rate of gases was calibrated through the use of a bubble displacement technique, which involved measuring rise time of a soap bubble in a 50-ml burette. The prepared flue gas composed of 79-82 % nitrogen, 12 % carbon dioxide, 5 % oxygen, and 1-3% sulphur dioxide by volume.

4.5 EXPERIMENTAL PROCEDURE

In the beginning of the experiment the reactant specimen was placed in the wire mesh basket and lowered into the furnace. The furnace was then purged nitrogen gas till it was brought to the reaction temperature and no further change was observed both in temperature and weight of the reactant pellet. The simulated flue gas was then turned on and a recording taken of the weight change with time. A direct reading multi gas analyzer (MIR-9000) measured the concentration of sulphur dioxide in the inlet and outlet gas. It may be mentioned here that the concentration of sulphur dioxide in the gas mixture, as measured by the gas analyser, was within 5 percent of that estimated from the flow rate through the calibrated capillary tube.

4.6 PORE VOLUME AND BET SURFACE AREA

The pore volume of the pellet was determined as suggested by Smith (1981) by boiling the pellets of known weight in benzene. After boiling for a period of ten minutes the sample was superficially dried and weighted. The increase in weight divided by the volume of benzene gives the pore volume of solid pellet. The porosity of the pellet can be calculated by dividing the pore volume by the total volume of the pellet.

BET surface area of the solid pellets under various conditions reported in the study was determined by a BET surface area analyzer (Model No. SA-3100, Coulter Company, England). The values have been reported in Table-A.1 (Appendix-A).

5. RESULTS AND DISCUSSION

In the present study it was decided to use the thermogravimetric method for studying the sulphation kinetics of the solid reactant (sodium carbonate obtained by thermal decomposition of sodium bicarbonate pellet). From thermodynamic considerations, the sulphation reaction may lead to the formation of sulphite or sulphate or a combination of both depending on the amount of oxygen present during the reaction. The fractional conversion (X) for sulphation reaction has been calculated from the weight change data assuming the end product to be sulphate. It was decided to conduct the experiments at a gas velocity of 4 cm/s, because above that the conversion is not affected by the gas velocity of the system, which indicates the absence of external mass transfer (Sohn and Szekely, 1972).

5.1 EFFECT OF TEMPERATURE ON SULPHATION

Experiments were conducted using cylindrical pellets of same diameter and height so that these can be approximated as spheres. The sulphur dioxide concentration was kept as 1.5 %. The experimental results are shown in table A.2 (Appendix-A) and the corresponding plot in Figure 5.1. It can be observed from the figure that conversion increased with temperature from 150 to 200 °C and decreased significantly at 350 °C. The increase in conversion is due to increased reaction rate at higher temperature. However the significant decrease at 350 °C may be due to sintering effects which offset the increased reaction rate in that range.

5.2 DETERMINATION OF ORDER OF REACTION

Though in general it is mentioned in the literature that the sulphation reaction follows first order kinetics with respect to sulphur dioxide concentration, it is essential to determine the order of reaction, as it is an important parameter for determining the rate of
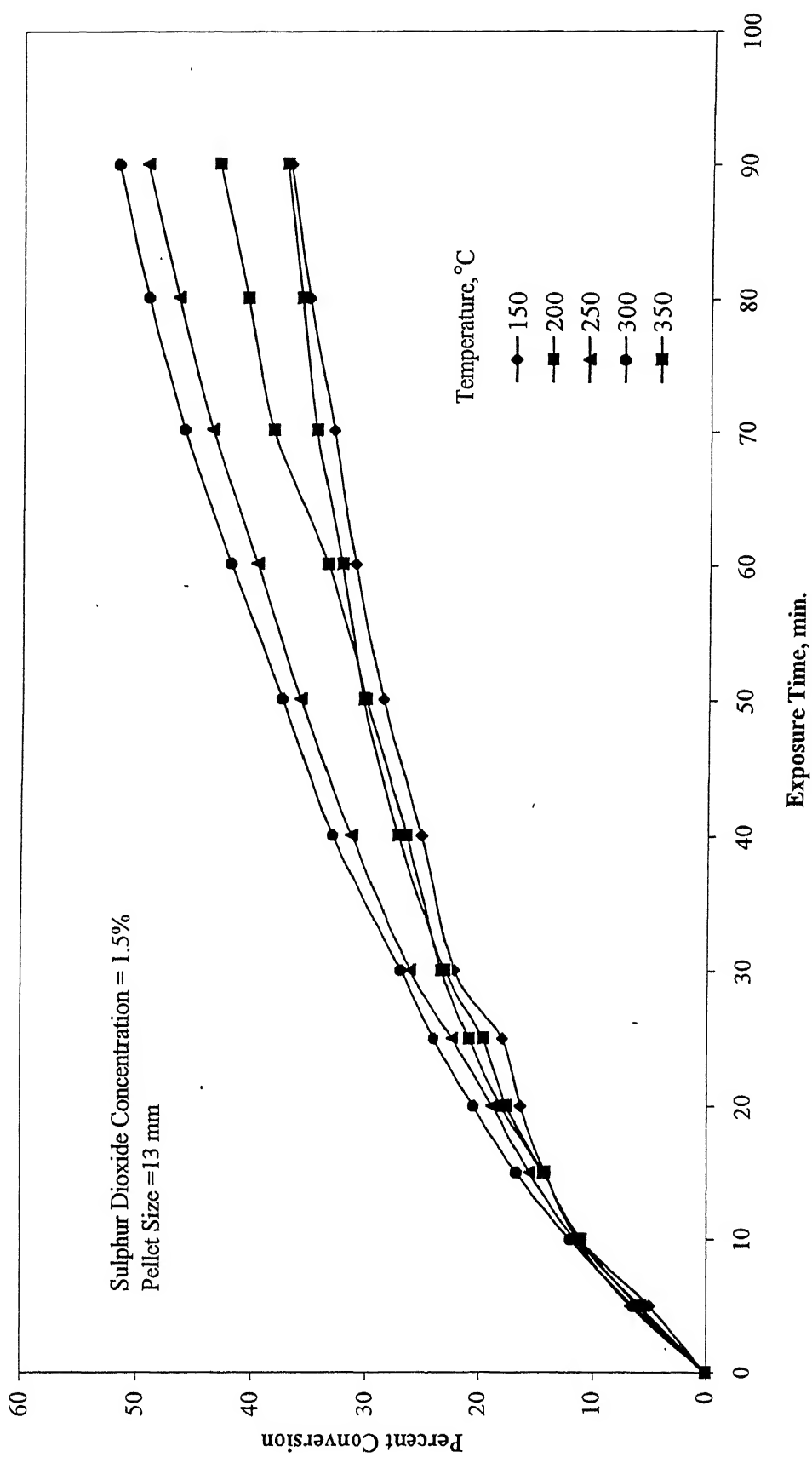
Fig. 5.1 Effect of Temperature on Sulphation Reaction

reaction. For finding the order of reaction thermogravimetric data were generated at different sulphur dioxide concentrations. Table A.3 shows the experimental data of conversion with time at different concentrations ranging from 0.25 to 2.25 %. The conversion function $[1-(1-X)^{1/3}]$ at different reaction times, assuming the chemical reaction as the rate limiting step, is shown in Table A.4. The conversion function versus time curves for different concentrations of sulphur dioxide are shown in Figure 5.2. The slope (S) determined from the initial rates in Figure 5.2 are reported in Table A.5.

The slope S can be written as

$$S = k'C^n$$

Where k' is a constant, C is the concentration of sulphur dioxide, and n is the order of reaction. The above equation can also be written as

$$\ln(S) = \ln(k') + n \ln(C)$$

From the values of sulphur dioxide concentration and the corresponding slopes, ln(S) versus ln(C) graph was plotted as shown in Figure 5.3. The slope of this curve (which is a best-fit straight line) gives the order of reaction. The slope was found to be 1.0678, which implies the reaction is of first order with respect to sulphur dioxide concentration.

5.3 EVALUATION OF INTRINSIC RATE CONSTANT

The intrinsic reaction rate constant k was obtained from the chemical reaction rate-controlling model represented by equation 2.5. The conversion function $[1-(1-X)^{1/3}]$ versus time curves at different temperature were plotted (Fig. 5.4) as per data given in Table A.6. In view of non-linearity of the plots the rate constant was calculated based on the initial slopes where diffusion effects are negligible. The initial slope (m) of these curves were found and are reported in Table A.7. The way of calculation is shown in Appendix-B. The intrinsic reaction rate constant was found to vary from 1.24×10^{-4} to 3.75×10^{-4} cm/s in the temperature range of 150 to 250 °C.
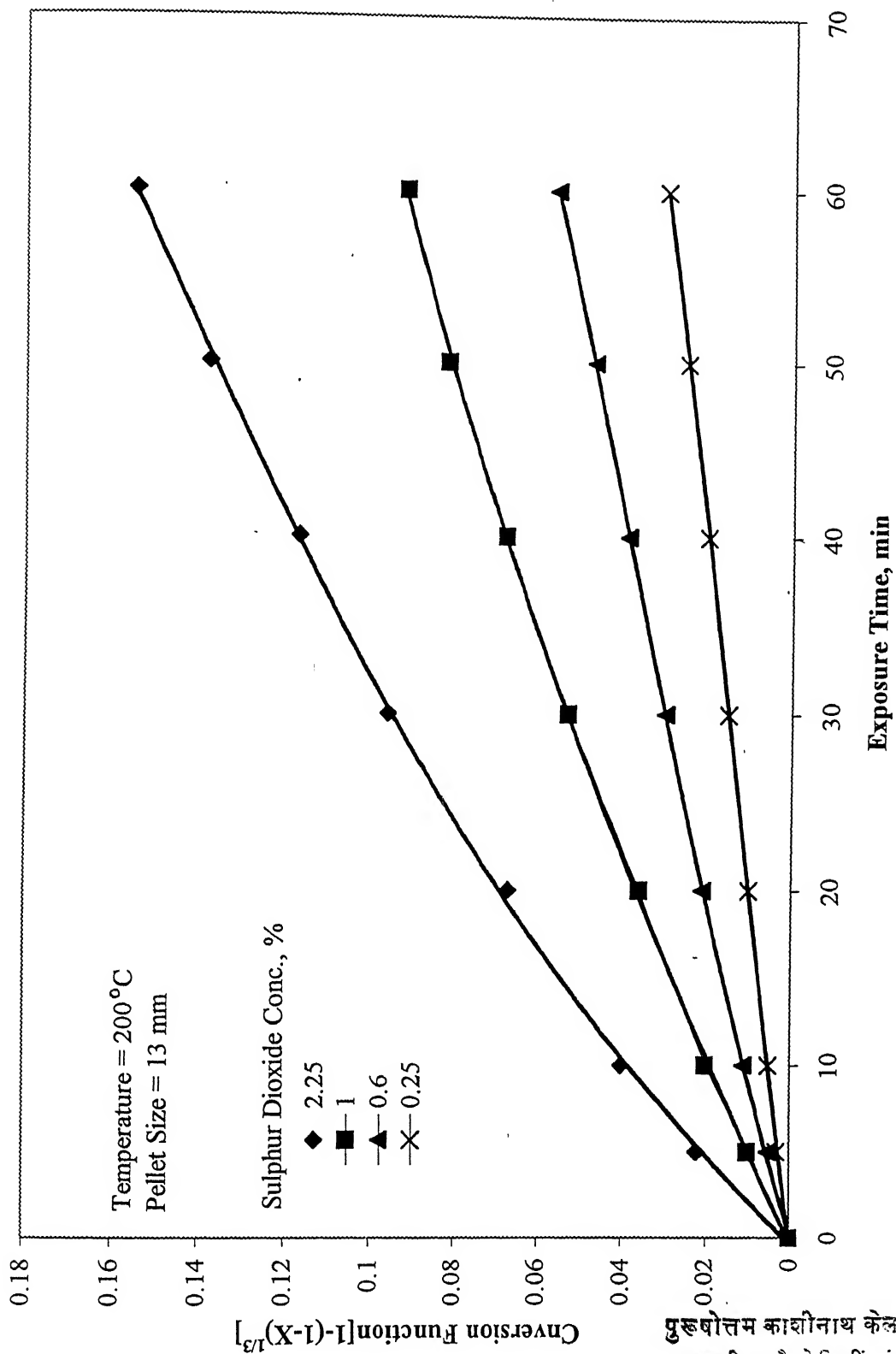
Fig. 5.2 Effect of Sulphur Dioxide Concentration on Sulphation Reaction

Temperature = 200°C
Pellet Size = 13 mm

Sulphur Dioxide Conc., %

♦ 2.25
■ 1
▲ 0.6
✕ 0.25

Conversion Function $[1-(1-X)^{1/3}]$

Exposure Time, min
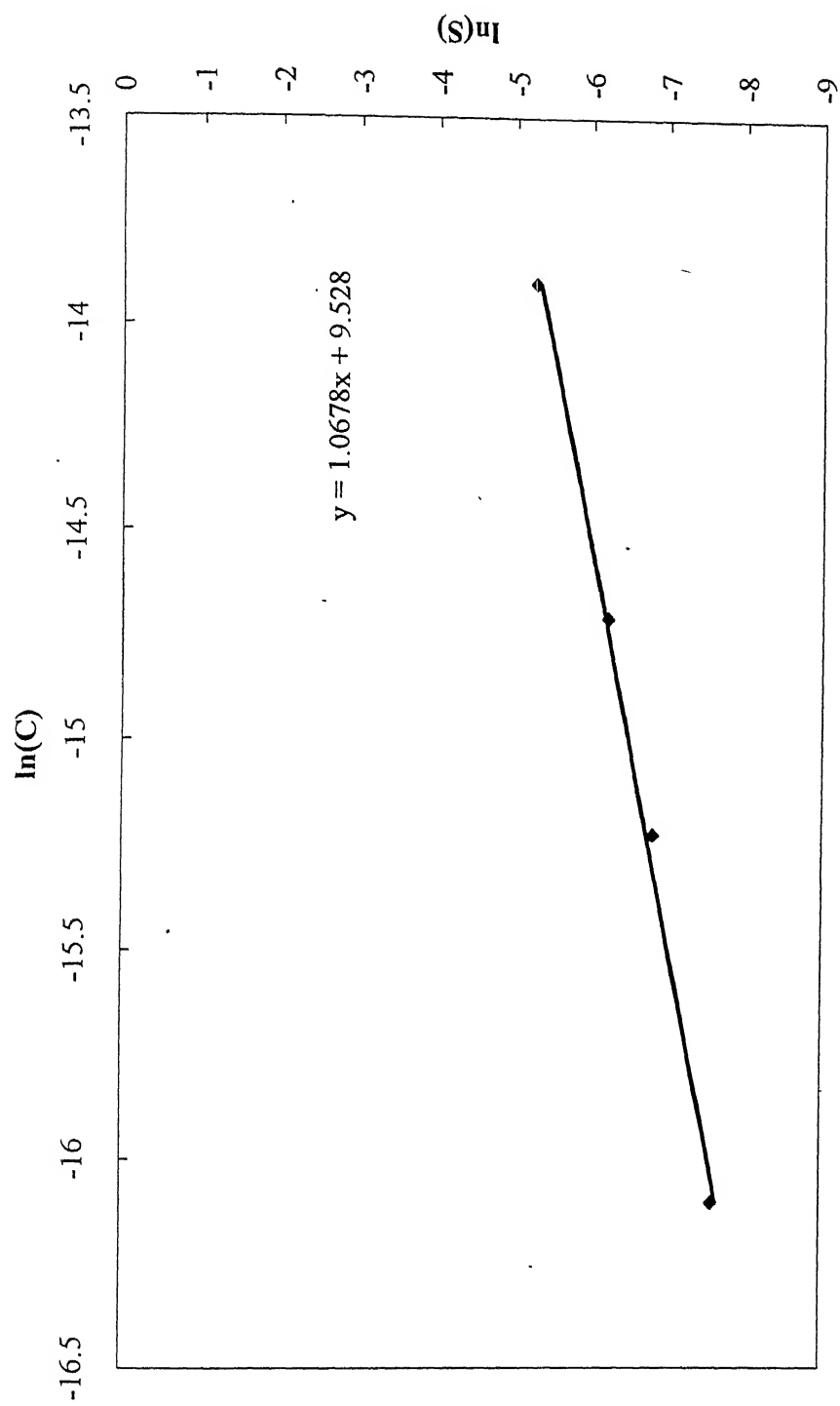
Fig 5.3 Plot for Detremining the Order of Reaction

$$y = 1.0678x + 9.528$$

Fig. 5.4 Chemical Reaction Model for Sulphation Reaction at Different Temperatures

5.4 TEMPERATURE DEPENDENCY OF RATE CONSTANT

The temperature dependency of the rate constant is given by the Arrhenius relation: $k = A e^{(-E/RT)}$; where R is the universal gas constant = 1.99 Cal / K.mole, T is the absolute temperature in Kelvin, A and E are constants known as activation energy and frequency factor respectively.

The above relationship can also be written as: $\ln(k) = \ln(A) - E/RT$.

By knowing the values of the constants A and E one can find reaction rate (k) at any temperature. These constants for the sulphation reaction can be determined by plotting ln(k) versus 1/T graph as shown in Figure 5.5 (data given in Table A.7). Slope of this curve gives the activation energy (E) and the y-intercept gives the frequency factor (A), which were found to be 4368 Cal/mole and 0.0217 cm/s, respectively.

5.5 DETERMINATION OF EFFECTIVE DIFFUSIVITY

The conversion data with time at different temperatures as reported in Table A.8 were used to find the effective diffusivity. Using these data the values of conversion function $[1-3(1-X)^{2/3}+2(1-X)]$ was calculated according to the pore diffusion model given by equation 2.6 and are shown in the same table . In order to find the diffu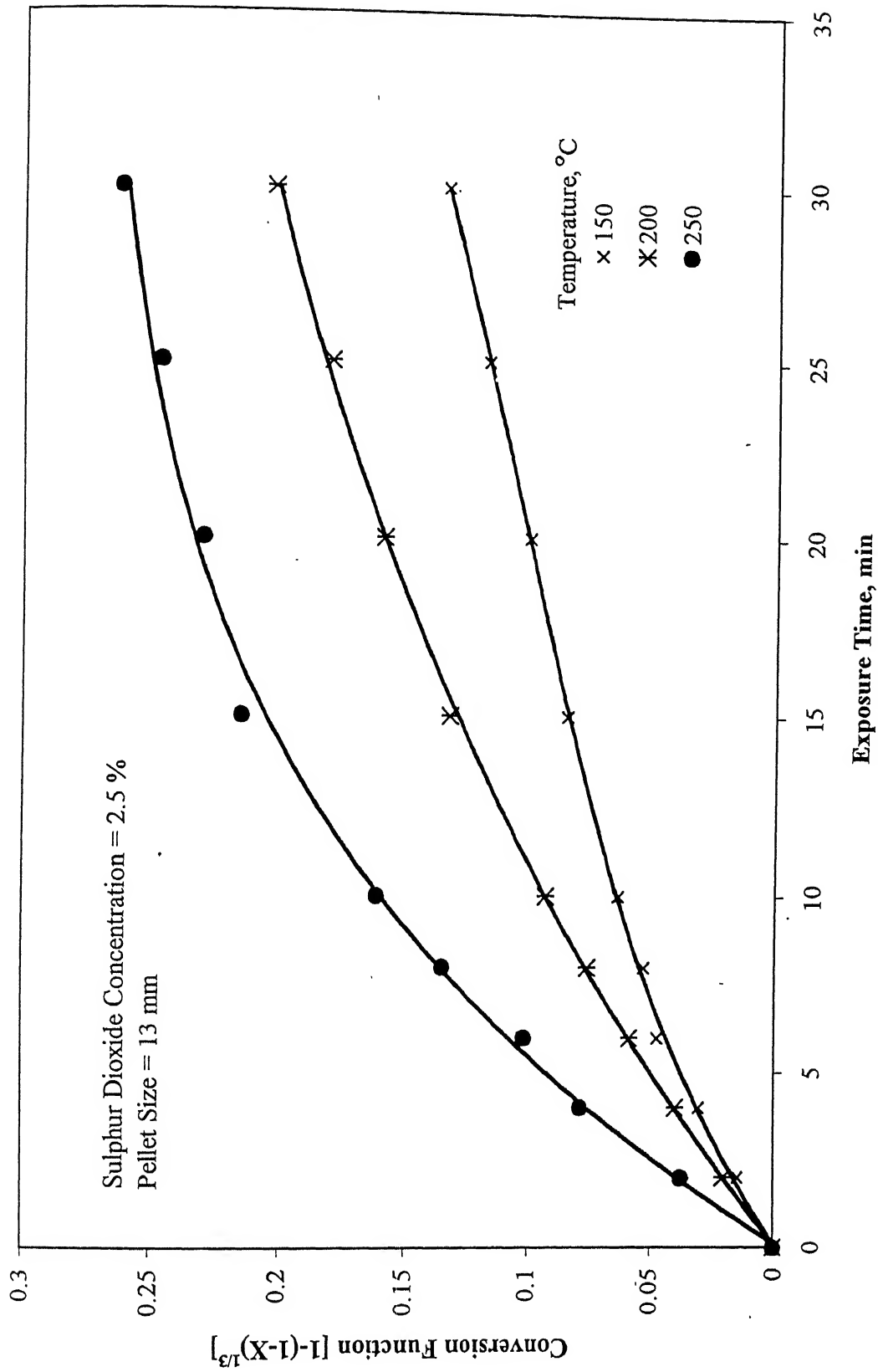sion effects at different temperatures, the conversion function versus exposure time was plotted as shown in Figure 5.6. It can be observed from the plot that the data fits a straight line, except for the initial period where chemical reaction may be controlling the rate. From the slope of the linear portion of the plot and using Eq. 2.6 with appropriate manipulations, the effective diffusivity (D_e) in the product layer was determined and reported in Table A.9. (Calculation showed in Appendix C). D_e was found to be increasing with temperature. It varied from 0.0089 to 0.0187 cm^2/s in the temperature range of 150 to 250 °C. The value of reaction modulus (σ) was found to vary from 3.40 to 3.72 in the temperature range of 150 to 250 °C indicating strong influence of pore diffusion on the progress of the reaction (Sohn and Szekely, 1972).

24
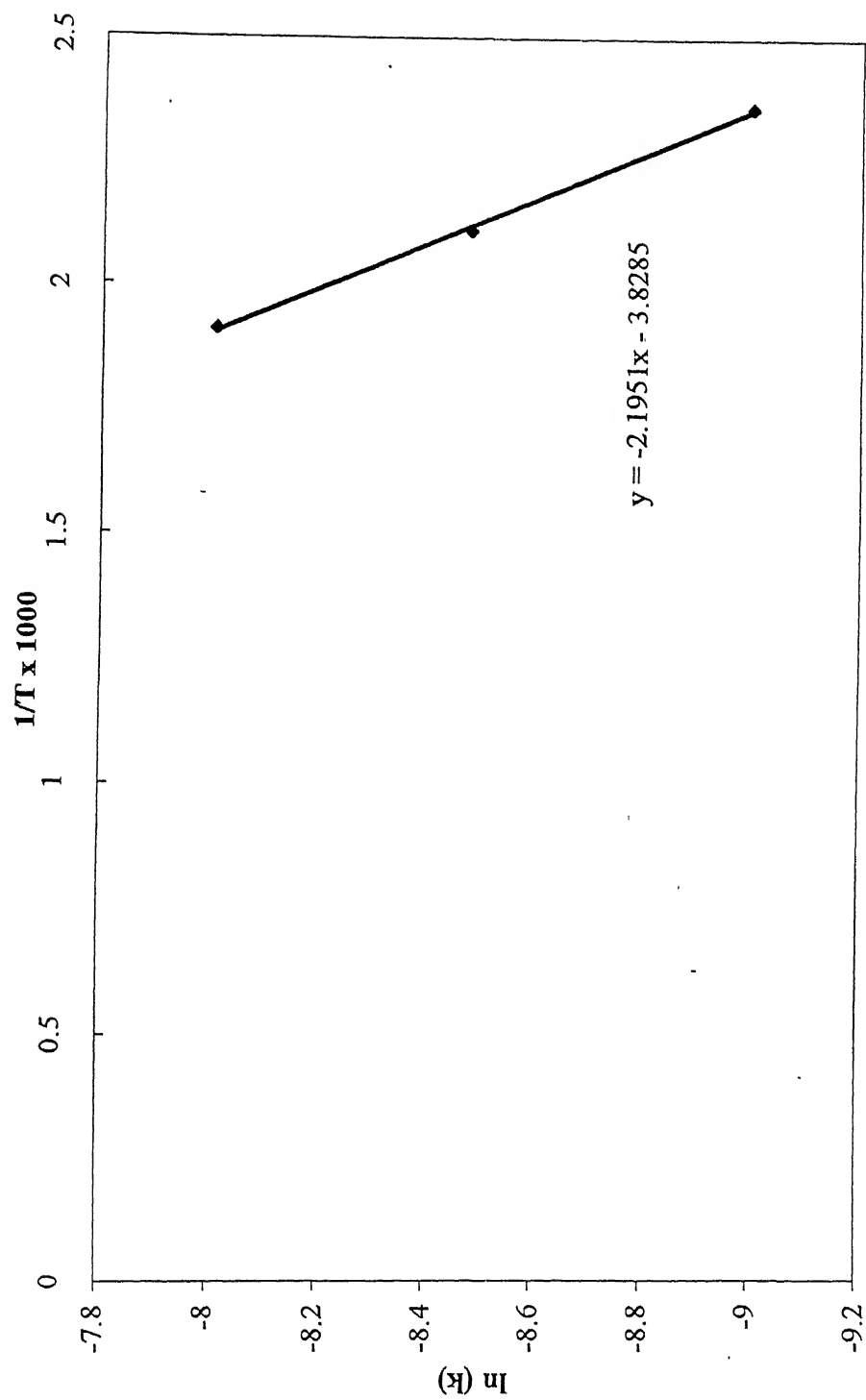
Fig. 5.5 Arrhenius Plot for the Sulphation Reaction

$y = -2.1951x - 3.8285$
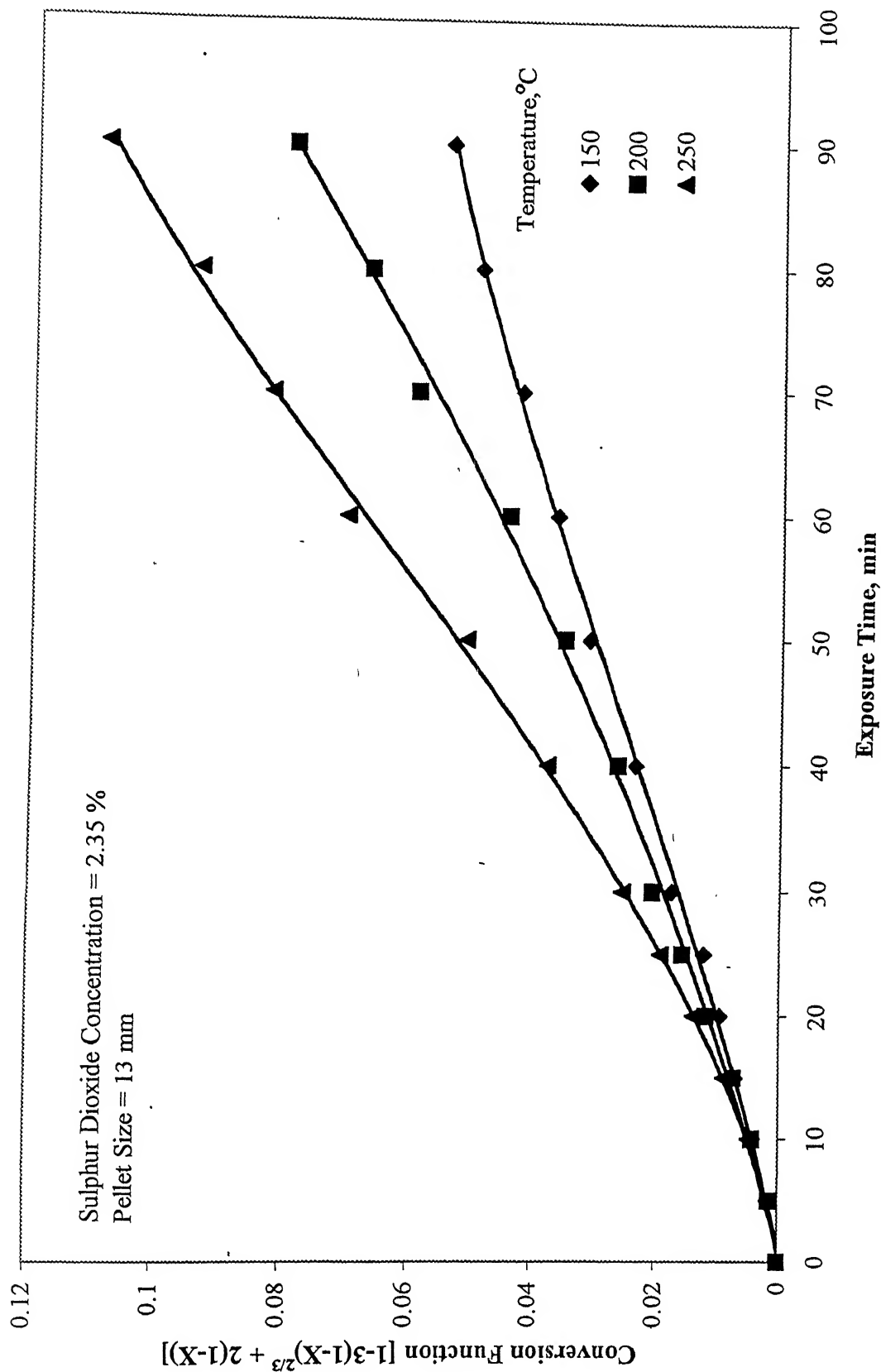
Fig. 5.6 Pore Diffusion Model for Sulphation Reaction at Different Temperature

26

5.6 TESTING THE MODELS WITH EXPERIMENTAL DATA

An attempt was made to fit the experimental conversion data with the predicted conversion, based on the chemical reaction and pore diffision models mentioned in the earlier chapter. The values of dimensionless reaction time for different conversion using different models were calculated and are shown in Table A.10 for a particular set of experimental conditions. The theoretical curves of fractional conversion versus dimensionless time for the two models along with the experimental conversion are shown in Figure 5.7. It can be observed from the figure that the experimental data matched with the chemical reaction model for a very small initial period of reaction. As the reaction progresses the experimental data matched with the pore diffusion model.

Sulphur Dioxide Concentration = 2.35%
Temperature = 150 °C
Pellet Size = 13 mm

◆ Experimental Data
Chemical Reaction Model
Pore Diffusion Model

Dimensionless Time (t*)

Fractional Conversion (X)
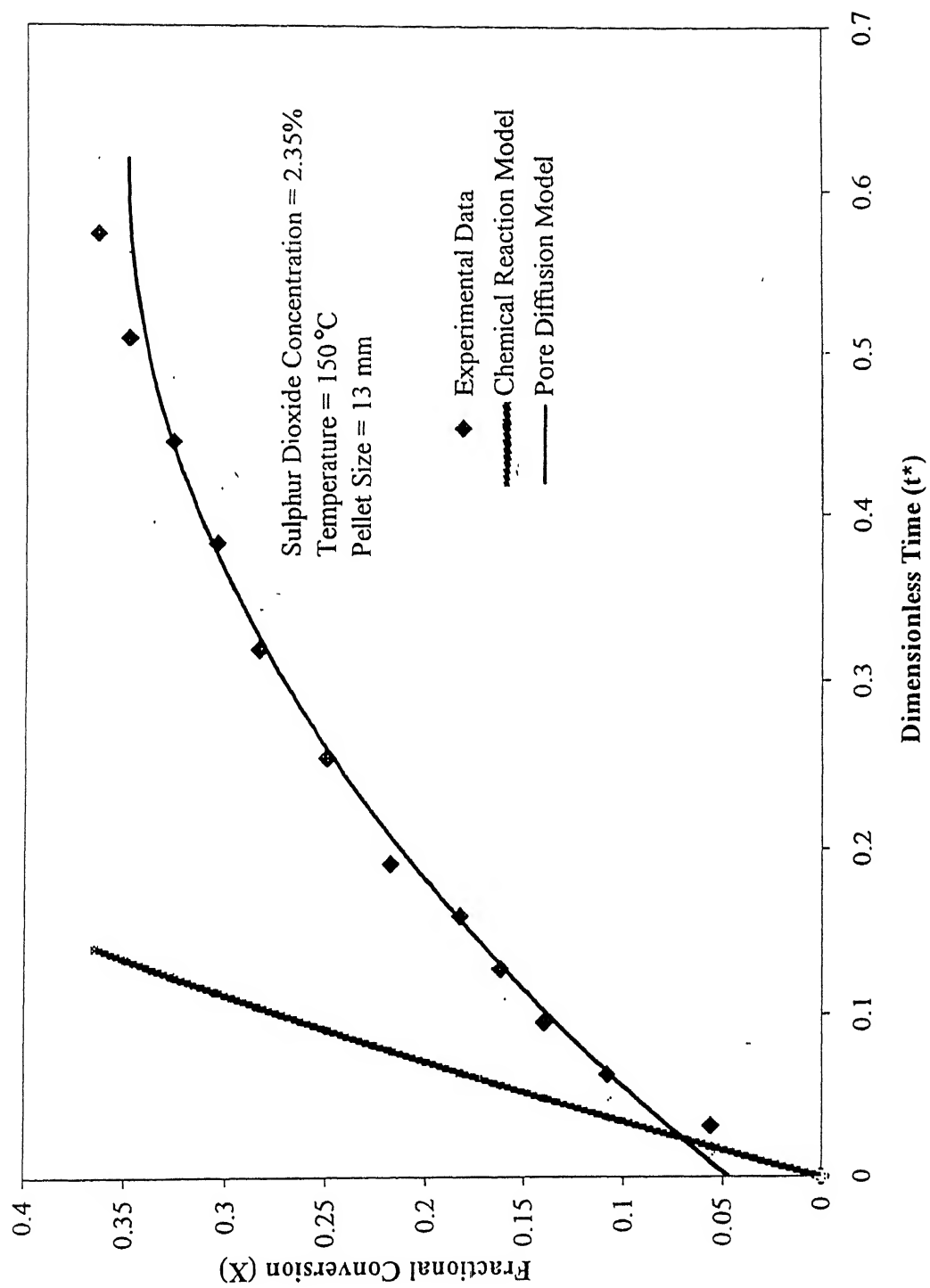
Fig. 5.7 Predicted Conversion and Experimental Data

6. SUMMARY AND SUGGESTIONS

- Sodium carbonate (obtained from thermal decomposition of sodium bicarbonate pellet) can be advantageously used for dry flue gas desulphurisation.

- The intrinsic rate constant for the sulphation reaction was found to vary from 1.24×10^{-4} to 3.75×10^{-4} cm/s in the temperature range of 150 to 250 °C.

- The activation energy and frequency factors were found to be 4368 Cal/mole and 0.027 cm/s respectively.

- The effective diffusivity was found to vary from 8.9×10^{-3} to 18.7×10^{-3} cm^2/s in the temperature range of 150 to 250 °C.

- Application of the different models indicated that the sulphation reaction of the solid reactant was controlled by chemical reaction for a short initial period and then strongly by pore diffusion with the progress of reaction.

The sodium carbonate obtained by thermal decomposition of sodium bicarbonate is highly porous and thus it is extremely reactive towards sulphur dioxide. High degree of desulphurisation can be achieved by injecting solid, dry and fine-grained sodium bicarbonate in hot gas stream at appropriate place in a desulphurisation unit. The performance of this porous solid reactant may also be tested both theoretically and practically in fixed and fluidized bed reactors. Appropriate models may be developed for predicting the performance of these solid reactants in the above mentioned reactors.

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APPENDICES

APPENDIX-A

Table A.1 Experimentally Measured Physical Parameters of Solid Reactant

Decomposition Temperature (^{o} C)	Pore Volume (cm^3/gm)	Porosity	BET Surface Area (m^2/gm)
150	0.49	0.55	3.14
200	0.47	0.53	2.70
250	0.46	0.52	2.50

Table A.2 Data for the Effect of Temperature on Sulphation Reaction

Exposure Time (min.)	Percent Conversion at Different Temperature			
	150 °C	200 °C	250 °C	300 °C
0	0	0	0	0
5	4.97	5.95	6.58	6.35
10	11.02	10.98	11.48	11.93
15	14.12	14.26	15.49	16.63
20	16.31	18.01	18.76	20.40
25	17.92	20.78	22.28	23.92
30	22.08	23.29	26.02	26.88
40	25.11	26.41	31.21	32.95
50	28.57	30.07	35.86	37.43
60	31.12	33.52	39.68	41.96
70	32.98	38.27	43.58	46.04
80	35.12	40.51	46.53	49.15
90	36.79	42.97	49.26	51.72

Sulphur Dioxide Concentration = 1.5%

Table A.3 Data for the Effect of SO$_2$ Concentration on Sulphation Reaction

Exposure Time (min.)	Percent Conversion at Different SO$_2$ Concentration			
	2.25%	1.00%	0.60%	0.25%
0	0	0	0	0
5	6.58	2.96	1.48	0.90
10	11.48	5.85	3.35	1.52
20	18.76	10.50	6.12	3.01
30	26.02	15.06	8.75	4.50
40	31.21	19.04	11.30	5.86
50	35.86	22.52	13.58	7.42
60	39.68	25.10	15.75	8.74

Temperature = 200 °C

Table A.4 Data for Chemical Reaction Model at Different SO_2 Concentration

Exposure Time (min.)	Conversion Function $[1-(1-X)^{(1/3)}]$ at Different SO_2 Concentration			
	2.25%	1.00%	0.60%	0.25%
0	0	0	0	0
5	0.022	0.010	0.005	0.003
10	0.040	0.020	0.011	0.005
20	0.067	0.036	0.021	0.010
30	0.096	0.053	0.030	0.015
40	0.117	0.068	0.039	0.020
50	0.138	0.082	0.047	0.025
60	0.155	0.092	0.056	0.030

Temperature = 200 °C

Table A.5 Data for Determining the Order (n) of Reaction

Slope (S)	C X 10^7	ln(S)	ln(C)
0.0052	9.18	-5.26	-13.90
0.0020	4.08	-6.21	-14.71
0.0011	2.45	-6.81	.-15.22
0.0005	1.02	-7.60	-16.10

Table A.6 Data for Chemical Reaction Model for Sulphation Reaction at Different Temperatures

Exposure Time (min.)	Fractional Conversion (X) at Different Temperature			Conversion Function $[1- (1-X)^{(1/3)}]$		
	150 °C	200 °C	250 °C	150 °C	200 °C	250 °C
0	0	0	0	0	0	0
2	0.043	0.060	0.108	0.015	0.020	0.037
4	0.088	0.114	0.216	0.030	0.040	0.078
6	0.135	0.165	0.274	0.047	0.058	0.101
8	0.150	0.210	0.352	0.053	0.076	0.135
10	0.178	0.253	0.410	0.063	0.093	0.161
15	0.232	0.347	0.516	0.084	0.132	0.215
20	0.265	0.405	0.544	0.010	0.159	0.230
25	0.312	0.449	0.573	0.117	0.180	0.247
30	0.350	0.493	0.598	0.134	0.203	0.262

SO_2 Concentration = 2.5%

Table A.7 Evaluation of Rate Constant (k) and Data for Determining Arrhenius Constants A and E.

Temperature,T ($^{\circ}$K)	Slope(m)X 10^4	k X 10^4	1000/T	ln(k)
423	1.39	1.24	2.36	-9.00
473	2.08	2.17	2.11	-8.48
523	3.33	3.75	1.91	-8.01

b=1, Fg=3, ρ=0.0239 g.mol/cm^3, C=1.02X10^{-6} g.mol/cm^3

Table A.8 Data for Pore Diffusion Model for Sulphation Reaction at Different Temperatures

Exposure Time (min.)	Fractional Conversion (X) at Different Temperature			Conversion Function $1 - 3(1-X)^{(2/3)} + 2(1-X)$		
	150 °C	200 °C	250 °C	150 °C	200 °C	250 °C
0	0	0	0	0	0	0
5	0.0557	0.0625	0.0676	0.0011	0.0013	0.0016
10	0.1079	0.1102	0.1150	0.0041	0.0043	0.0047
15	0.1396	0.1435	0.1557	0.0069	0.0073	0.0087
20	0.1618	0.1798	0.1935	0.0094	0.0117	0.0137
25	0.1823	0.2065	0.2265	0.0121	0.0157	0.0191
30	0.2174	0.2331	0.2579	0.0175	0.0203	0.0252 ·
40	0.2493	0.2633	0.3098	0.0234	0.0263	0.0374
50	0.2833	0.2993	0.3554	0.0308	0.0347	0.0506
60	0.3045	0.3338	0.4005	0.0360	0.0440	0.0698
70	0.3265	0.3813	0.4374	0.0420	0.0591	0.0820
80	0.3491	0.4023	0.4671	0.0486	0.0667	0.0939
90	0.3649	0.4329	0.4970	0.0536	0.0788	0.1086

Sulphur Dioxide Concentration = 2.35%

Table A.9 Evaluation of Effective Diffusivity (De) and Reaction Modulus (σ)

Temperature °C	m X10^4	s X10^4	$\sigma=(m/s)^{0.5}$	De (cm^2/s)
150	1.39	0.12	3.40	0.0089
200	2.08	0.17	3.50	0.0129
250	3.33	0.24	3.72	0.0187

Table A.10 Predicted Conversion and Experimental Data

Exposure Time, t (min.)	Fractional Conversion, X	t^* (Experimental) $= Z \cdot t$	t^* (Chemical Reaction Model) $= [1-(1-X)^{1/3}]$	t^* (Pore Diffusion Model) $=[1 - 3(1-X)^{(2/3)} + 2(1-X)]$
0	0	0	0	0
5	0.0557	0.0319	0.0189	0.0127
10	0.1079	0.0638	0.0373	0.0474
15	0.1396	0.0957	0.0489	0.0705
20	0.1618	0.1275	0.0571	0.1087
25	0.1823	0.1594	0.0649	0.1399
30	0.2174	0.1913	0.0785	0.2023
40	0.2493	0.2551	0.0911	0.2705
50	0.2833	0.3188	0.1051	0.3560
60	0.3045	0.3826	0.1140	0.4162
70	0.3265	0.4464	0.1234	0.4850
80	0.3491	0.5101	0.1334	0.5618
90	0.3649	0.5739	0.1404	0.6199

Temperature = 150 °C
Sulphur Dioxide Concentration = 2.35%
Reaction Modulus, σ=3.40 at 150 °C

Note : (For Experimental Data)
$t^* = (bkCAg/\rho FgVg)t$
$b=1$, $Fg=3$, $Ag=3.14 \times 10^{-4}$, $Vg=0.49$, $k=1.24 \times 10^{-4}$, $C=9.59 \times 14 \times 10^{-7}$, $\rho=0.0239$ (Units are as defined in Equation 2.5)
Substituting, $t^* = (0.006377)t = Z.t$; t =Exposure time in minute.

APPENDIX –B

CALCULATION FOR INTRINSIC REACTION RATE CONSTANT

The intrinsic reaction rates were calculated from the initial slopes where the diffusional effects are negligible. The way of calculation is shown below. It is calculated from chemical reaction rate controlling model using the value of the slope.

$$t^* = 1 - (1-X)^{\frac{1}{3}}$$

or $\quad [1 - (1-X)^{\frac{1}{3}}] = mt$

where $\quad m$ = slope of curve (from figure 5.4) $= \dfrac{bkCA_g}{\rho F_g V_g}$

$\therefore k = \dfrac{m\rho F_g V_g}{bCA_g}$

APPENDIX-C

CALCULATION FOR REACTION MODULUS AND EFFECTIVE DIFFUSIVITY

The effective diffusivity was calculated from the pore diffusion model by Equation 2.6 and using other physical parameters of the solid reactant. The reaction modulus was calculated from the slope of the curve shown in figure 5.6.

$$t^* = \sigma^2[1 - 3(1 - X)^{\frac{2}{3}} + 2(1 - X)]$$

$$t = (\sigma^2 / m)[x + (1 - x)\ln(1 - x)]$$

$$\sigma = (V_p / A_p)[(1 - \varepsilon_0)kA_gF_p / 2D_eF_gV_g]^{\frac{1}{2}}$$

$$\therefore D_e^{\frac{1}{2}} = (1 / \sigma)(V_p / A_p)[(1 - \varepsilon_0)kA_gF_p / 2F_gV_g]^{\frac{1}{2}}$$

where   m = slope of the curve for chemical reaction model (from Figure 5.4)

m/σ^2 = slope of the curve for pore diffusion model (from Figure 5.6).